Strong Metal–Oxygen Interaction in Uracils

X-RAY CRYSTAL STRUCTURE OF BIS-(1,3-DIMETHYLURACIL)DICHLOROCOPPER(II)

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An X-ray structure determination showed that in the compound bis-(1,3-dimethyluracil)-dichlorocopper(II) the uracil moiety is strongly bonded to the metal via the O₍₄₎ atom. Changes in the i.r. spectra on metal binding are discussed. Details of the structural parameters have been deposited as Supplementary Publication SUP 50091 (3 pages) at the British Library Lending Division, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, U.K., from whom copies can be obtained on the terms indicated in *Biochem. J.* (1978) 169, 5.

Work on the interactions of metal ions with the base components of nucleic acids has focused largely on the nitrogen-donor sites, and uracils, in which both nitrogens are protonated, have been somewhat neglected. The only crystallographic evidence for the binding of heavy metals to uracils comes from the structures of mercury complexes of uracil and dihydrouracil, which have very long and presumably weak metal–oxygen bonds (Carrabine & Sundaralingam, 1971; Hodgson, 1977), and from several complexes, prepared under basic conditions, in which the uracil is deprotonated and the metal bound to nitrogen.

We report here the structure of a copper(II) complex of 1,3-dimethyluracil in which the metal is bonded strongly to the C₍₄₎=O₍₄₎ group of the base. It is the first uracil derivative for which a powerful metal–oxygen interaction has been demonstrated, and is consistent with recent work (Goodgame & Johns, 1977) that shows that a variety of metal complexes of uracil and thymine may be prepared in weakly polar media.

Experimental

A hot saturated solution of CuCl₂·2H₂O (AnalaR; BDH Chemicals, Poole, Dorset, U.K.) (0.085 g) in ethanol was added to a hot solution of 1,3-dimethyluracil (prepared by the method of Davidson & Baudisch, 1926) (0.14 g) in ethyl acetate (20 ml). A clear solution was obtained, which on slow evaporation yielded crystals suitable for X-ray study. Microanalytical results (Microanalytical Laboratory, Imperial College) were: found: C, 33.79; H, 3.56; N, 13.80; calc. for Cu(C₆H₈N₂O₂)₂Cl₂: C, 34.75; H, 3.89; N, 13.51%.

Infrared spectra were obtained using Perkin–Elmer 257 and 457 spectrophotometers, and reflectance spectra using a Beckman DK2A recording spectrophotometer. All measurements were at room temperature.

Preliminary oscillation and Weissenberg photographs showed the green ribbon-like crystals to be triclinic. Possible space groups were *P*1 or *P* $\bar{1}$, the latter was shown to be correct by the subsequent successful refinement. Accurate unit-cell dimensions were obtained by measuring 28 high-angle reflexions on a diffractometer and performing a least-squares calculation, to give *a* = 1.2028(1), *b* = 0.8449(1), *c* = 0.3883(1) nm [*a* = 12.028(1), *b* = 8.449(1), *c* = 3.883(1) Å], α = 93.66(1), β = 93.69(1), γ = 101.27(1)°, at 10°C, *U* = 0.3850 nm³ [*U* = 385.0 Å³], and *Z* = 1. (Throughout this paper standard deviations are given in parentheses after the various parameters.) Intensities of 1155 independent reflexions (to θ = 60°) were measured with CuK α radiation on a Siemens off-line automatic four-circle diffractometer. Of these, 221 were considered ‘unobserved’ as the net count of each was less than 2.58 σ (Allen *et al.*, 1971). The data were corrected for absorption, and the structure was solved by the heavy-atom method. Full-matrix least-squares refinement has reached *R* = 0.034.

Description of the structure and discussion

Fig. 1 shows the molecular structure found for bis-(1,3-dimethyluracil)dichlorocopper(II). Details of the molecular structure have been deposited as Supplementary Publication SUP 50091 (3 pages) at the British Library Lending Division, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, U.K., from whom copies can be obtained on the terms indicated

Fig. 1. Structure of bis-(1,3-dimethyluracil)dichlorocopper(II)

Table 1. Infrared spectra ($1600\text{--}1730\text{ cm}^{-1}$) of some uracil derivatives

	Wavenumber (cm^{-1})			Reference
	1720	1675	1645	
Uracil				(Mansy & Tobias, 1975)
Bisuracildichloromercury(II)	1722	1678	1643	(Mansy & Tobias, 1975)
1,3-Dimethyluracil	1708	1655 (broad)		Present work
Bis-(1,3-dimethyluracil)dichlorocopper(II)	1717	1647	1604	Present work

in *Biochem. J.* (1978) 169, 5. The copper atom lies on a centre of symmetry, and is bonded to two *trans* chlorine atoms and to two 1,3-dimethyluracil moieties via the $\text{O}_{(4)}$ position. $\text{Cu}\text{--}\text{Cl}$ and $\text{Cu}\text{--}\text{O}$ bond lengths are $0.2269(1)\text{ nm}$ [$2.269(1)\text{ \AA}$] and $0.1985(3)\text{ nm}$ [$1.985(3)\text{ \AA}$] respectively, and both are typical of strong bonds. By symmetry the copper atom has a strictly planar co-ordination, with $\text{O}\text{--}\text{Cu}\text{--}\text{Cl}$ angles of $88.5(1)$ and $91.5(1)^\circ$. The two pseudo-octahedral positions are occupied by chlorine atoms from neighbouring molecules, with long $\text{Cu}\cdots\text{Cl}$ distances of $0.295(1)\text{ nm}$ [$2.95(1)\text{ \AA}$]. Inter-molecular packing of the 1,3-dimethyluracil moieties is such that the separation between base planes is $0.339(1)\text{ nm}$ [$3.39(1)\text{ \AA}$], typical of structures where base-stacking occurs.

Structures of the two mercury derivatives, bisuracildichloromercury(II) and bis(dihydrouracil)dichloromercury(II), show only weak, secondary metal- $\text{O}_{(4)}$ bonding, with $\text{Hg}\text{--}\text{O}$ distances of $0.271(2)\text{ nm}$ [$2.71(2)\text{ \AA}$] and $0.288(3)\text{ nm}$ [$2.88(3)\text{ \AA}$] respectively (Carrabine & Sundaralingam, 1971). In line with this weak interaction the $\text{C}_{(4)}\text{--}\text{O}_{(4)}$ distance in the ligand, $0.125(3)\text{ nm}$ [$1.25(3)\text{ \AA}$], is not significantly changed compared with that found in uracil itself, $0.1245(2)\text{ nm}$ [$1.245(2)\text{ \AA}$] (Stewart & Jensen, 1967). Comparison of bond lengths in bis-(1,3-dimethyluracil)dichlorocopper(II) with those of

1,3-dimethyluracil itself (Banerjee *et al.*, 1977) shows that even strong metal-oxygen binding results in only small changes of $\text{C}=\text{O}$ bond lengths, $\text{C}_{(2)}=\text{O}_{(2)}$ being slightly shortened, $0.1212(5)\text{ nm}$ [$1.212(5)\text{ \AA}$] compared with $0.1225(3)\text{ nm}$ [$1.225(3)\text{ \AA}$], and more significantly $\text{C}_{(4)}=\text{O}_{(4)}$ slightly lengthened, $0.1246(4)\text{ nm}$ [$1.246(4)\text{ \AA}$] compared with $0.1227(3)\text{ nm}$ [$1.227(3)\text{ \AA}$].

Infrared spectra in the carbonyl stretching region reflect these small changes. Compared with the ligand, the copper complex shows an increase in energy of one band, normally ascribed (Angell, 1961; Lord & Thomas, 1967) to $\nu(\text{C}_{(2)}=\text{O}_{(2)})$, and a decrease in energy of the other [$\nu(\text{C}_{(4)}=\text{O}_{(4)})$ with admixture of ring modes] (see Table 1). The changes, however, are very small, especially in view of the breadth of the bands, and, although the shifts are larger for the strongly bonded copper complex than for the weakly bonded mercury one, careful measurements are necessary to distinguish the difference. Similar small changes have been observed in some uracil complexes (Goodgame & Johns, 1977), suggesting that these too may involve quite strong metal-oxygen bonding.

The electronic reflectance spectrum of bis-(1,3-dimethyluracil)dichlorocopper(II) shows only one band in the visible and near-infrared region, with a maximum at 12100 cm^{-1} . This is low for a planar CuO_2Cl_2 chromophore having little interaction with fifth and sixth ligands (Hathaway, 1972), in agreement with the weak ligand field found for uracil (Goodgame & Johns, 1977). The structure of bis-(1,3-dimethyluracil)dichlorocopper(II) shows that this is not due to weakness of the metal-oxygen bond. One possible explanation for it would be the presence of some π -bonding from oxygen to copper. This would be consistent with the fact that high π -electron densities have been calculated for both oxygen atoms of uracil (Kulakowska *et al.*, 1974), and with the relatively large $\text{C}\text{--}\text{O}\text{--}\text{Cu}$ angle of the present structure [$133.5(2)^\circ$].

In bis-(1,3-dimethyluracil)dichlorocopper(II) the short $\text{Cu}\text{--}\text{O}$ bond is not dictated by the stoichiometry, since a $4+2$ co-ordination of copper could have been achieved by chloride bridges and long $\text{Cu}\text{--}\text{O}$ bonds. It may well be, therefore, that strong metal-oxygen bonding involving uracil species is more common than had been supposed. In this respect the use of i.r. spectra as a diagnostic criterion for the presence or absence of such bonding should be used with caution, since only the most accurate data will detect the small changes in $\nu(\text{C}=\text{O})$ that occur even with the strongest metal binding.

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